

5-Chloro-*N*-[2-(1*H*-imidazol-4-yl)ethyl]-*N*-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-amine

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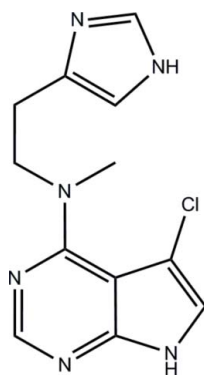
Received 17 December 2009; accepted 19 December 2009

Key indicators: single-crystal X-ray study; *T* = 208 K; mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$; *R* factor = 0.043; *wR* factor = 0.123; data-to-parameter ratio = 15.4.

The title compound, $\text{C}_{12}\text{H}_{13}\text{ClN}_6$, was prepared by reaction of 4,5-dichloro-7*H*-pyrrolo[2,3-*d*]pyrimidine with 2-(1*H*-imidazol-4-yl)-*N*-methylethanamine, and the X-ray study confirmed that chloro-substituent in six-membered ring was replaced in the reaction. The exocyclic N atom environment is approximately coplanar with the pyrrolo[2,3-*d*]pyrimidine [corresponding dihedral angle is $5.5 (1)^\circ$], whereas the mean plane of the N—C—C link connecting with the imidazolyl ring is almost exactly orthogonal to the plane of the bicyclic system [dihedral angle = $91.6 (2)^\circ$]. The imidazolyl plane itself, however, forms a relatively small dihedral angle of $20.8 (1)^\circ$ with the pyrrolo[2,3-*d*]pyrimidine plane. There are two independent N—H···N hydrogen bonds in the structure, which link molecules into layers parallel to $(\bar{1}03)$.

Related literature

For the structures of related compounds with the pyrrolo[2,3-*d*]pyrimidin-4-amine bicyclic framework, see: Abola & Sundaralingam (1973); Slauson *et al.* (2008); Zabel *et al.* (1987).



Experimental

Crystal data

| | |
|--|---|
| $\text{C}_{12}\text{H}_{13}\text{ClN}_6$ | $V = 1245.4 (2) \text{ \AA}^3$ |
| $M_r = 276.73$ | $Z = 4$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 4.4673 (5) \text{ \AA}$ | $\mu = 0.30 \text{ mm}^{-1}$ |
| $b = 15.8855 (17) \text{ \AA}$ | $T = 208 \text{ K}$ |
| $c = 17.6544 (19) \text{ \AA}$ | $0.16 \times 0.08 \times 0.08 \text{ mm}$ |
| $\beta = 96.244 (2)^\circ$ | |

Data collection

| | |
|--|--|
| Bruker SMART CCD area-detector diffractometer | 8932 measured reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | 2669 independent reflections |
| $T_{\min} = 0.953, T_{\max} = 0.976$ | 2223 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.029$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | 173 parameters |
| $wR(F^2) = 0.123$ | H-atom parameters constrained |
| $S = 1.05$ | $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$ |
| 2669 reflections | $\Delta\rho_{\min} = -0.55 \text{ e \AA}^{-3}$ |

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N2}-\text{H2}\cdots\text{N5}^i$ | 0.87 | 1.98 | 2.845 (2) | 175 |
| $\text{N6}-\text{H6A}\cdots\text{N3}^{ii}$ | 0.87 | 2.04 | 2.892 (2) | 167 |

Symmetry codes: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SIR97 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-32 (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2525).

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supplementary materials

Acta Cryst. (2010). E66, o242 [doi:10.1107/S1600536809054750]

5-Chloro-*N*-[2-(1*H*-imidazol-4-yl)ethyl]-*N*-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-amine

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Comment

The title compound, C₁₂H₁₃ClN₆, was prepared by reaction of 4,5-dichloro-7*H*-pyrrolo[2,3-*d*]pyrimidine with 2-(1*H*-imidazol-4-yl)-*N*-methylethanamine, and the present X-ray study confirmed that chloro-substituent in six-membered ring got replaced in this reaction (Fig. 1).

The pyrrolo[2,3-*d*]pyrimidine system is planar within 0.001 Å, and its least-squares plane, C1/C2/C3/C4/N2/C5/N3/C6/N1 is almost coplanar with the plane C1/N4/C7/C8, the corresponding dihedral angle being equal to 5.5 (1)° (the maximum deviation of the N4 atom from the latter plane being 0.028 (2) Å). The N4—C8—C9—C10 chain linking the bicyclic system with the imidazolyl group may be considered as approximately planar (within 0.130 Å) and its mean plane is orthogonal to the plane of pyrrolopyrimidine [91.6 (2)°]. At the same time the imidazolyl plane forms a relatively small dihedral angle of 20.8 (1)° with the bicyclic system.

The geometric parameters of pyrrolopyrimidin-4-amine system are similar to those observed in related structures (Zabel *et al.*, 1987; Abola & Sundaralingam, 1973), although the title compound provides the first structure with no substitution at the N atom in the pyrrole part. The only other structurally studied compound with disubstituted 4-amino-group (Slauson *et al.*, 2008) shows noticeable non-planarity of the environment of the exocyclic N atom.

There are two independent H-bonds in the structure (Table 1) which link molecules into layers parallel to (-1,0,3) plane (Fig. 2).

Experimental

To a mixture of 4,5-dichloro-7*H*-pyrrolo[2,3-*d*]pyrimidine (119 mg, 0.63 mmol) and [2-(1*H*-imidazol-4-yl)-ethyl]-methylamine (79 mg, 0.63 mmol) dissolved in 2-propanol (1 ml) was added di-isopropyl-ethylamine (0.12 ml, 1.1 eq). The reaction was heated at 80°C for 18 hrs. The solvent was removed and the reaction purified on Si—NH₂ (6% MeOH/EtOAc); product was isolated as colorless solid, 48 mg (27%). ¹H NMR (400 MHz, DMSO-*d*₆) δ p.p.m. 2.85 - 2.91 (m, 2 H), 3.22 (s, 3 H), 3.88 (dd, *J*=8.56, 6.80 Hz, 2 H), 6.78 (s, 1 H), 7.41 (d, *J*=1.76 Hz, 1 H), 7.52 (d, *J*=1.01 Hz, 1 H), 8.17 (s, 1 H), 12.05 (s, 1 H).

Refinement

All H atoms were placed in geometrically calculated positions (C—H 0.97 Å for methyl, 0.98 Å for methylene, 0.94 Å for aromatic CH-groups; N—H 0.87 Å) and included in the refinement in riding motion approximation. The *U*_{iso}(H) were set to 1.2*U*_{eq} of the carrying atom [1.5*U*_{eq} for methyl H atoms].

Figures

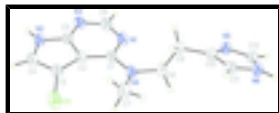


Fig. 1. Molecular structure of the title compound, showing 50% probability displacement ellipsoids and atom numbering scheme. H atoms are drawn as circles with arbitrary small radius.

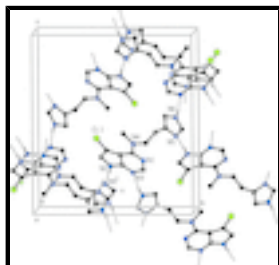


Fig. 2. Partial packing view of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bondings have been omitted for clarity. [Symmetry code: (i) $-x-1/2, y-1/2, -z+1/2$]

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Crystal data

$C_{12}H_{13}ClN_6$

$M_r = 276.73$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2yn$

$a = 4.4673$ (5) Å

$b = 15.8855$ (17) Å

$c = 17.6544$ (19) Å

$\beta = 96.244$ (2)°

$V = 1245.4$ (2) Å³

$Z = 4$

$F(000) = 576$

$D_x = 1.476$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4149 reflections

$\theta = 2.3$ – 27.6 °

$\mu = 0.30$ mm⁻¹

$T = 208$ K

Rod, colorless

$0.16 \times 0.08 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

phi and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

$T_{\min} = 0.953$, $T_{\max} = 0.976$

8932 measured reflections

2669 independent reflections

2223 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 27.7$ °, $\theta_{\min} = 1.7$ °

$h = -5 \rightarrow 2$

$k = -20 \rightarrow 19$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$wR(F^2) = 0.123$$

$$S = 1.05$$

2669 reflections

173 parameters

0 restraints

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.5128P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|--------------|----------------------------------|
| C1 | -0.0192 (4) | 0.58232 (11) | 0.29931 (10) | 0.0283 (4) |
| C2 | -0.1622 (4) | 0.50275 (10) | 0.28217 (10) | 0.0277 (4) |
| C3 | -0.1729 (4) | 0.41555 (11) | 0.30729 (11) | 0.0328 (4) |
| C4 | -0.3817 (4) | 0.37368 (12) | 0.25972 (11) | 0.0358 (4) |
| H4 | -0.4315 | 0.3165 | 0.2638 | 0.043* |
| C5 | -0.3795 (4) | 0.50431 (11) | 0.21665 (10) | 0.0297 (4) |
| C6 | -0.2998 (4) | 0.63935 (11) | 0.19349 (11) | 0.0351 (4) |
| H6 | -0.3424 | 0.6876 | 0.1634 | 0.042* |
| C7 | 0.2759 (5) | 0.53923 (14) | 0.41905 (14) | 0.0525 (6) |
| H7A | 0.0959 | 0.5146 | 0.4359 | 0.079* |
| H7B | 0.3892 | 0.5680 | 0.4614 | 0.079* |
| H7C | 0.3992 | 0.4952 | 0.4004 | 0.079* |
| C8 | 0.3331 (4) | 0.68204 (12) | 0.36897 (11) | 0.0346 (4) |
| H8A | 0.3273 | 0.7100 | 0.3194 | 0.042* |
| H8B | 0.5448 | 0.6750 | 0.3891 | 0.042* |
| C9 | 0.1773 (4) | 0.73809 (12) | 0.42332 (11) | 0.0339 (4) |
| H9A | -0.0034 | 0.7630 | 0.3957 | 0.041* |
| H9B | 0.1139 | 0.7035 | 0.4647 | 0.041* |
| C10 | 0.3803 (4) | 0.80697 (11) | 0.45646 (10) | 0.0297 (4) |
| C11 | 0.5339 (4) | 0.81184 (12) | 0.52734 (11) | 0.0344 (4) |
| H11 | 0.5279 | 0.7730 | 0.5673 | 0.041* |
| C12 | 0.6424 (4) | 0.92068 (12) | 0.45984 (11) | 0.0354 (4) |
| H12 | 0.7291 | 0.9715 | 0.4459 | 0.042* |
| N1 | -0.0952 (3) | 0.64914 (9) | 0.25352 (9) | 0.0331 (3) |
| N2 | -0.5079 (3) | 0.42744 (9) | 0.20513 (9) | 0.0336 (3) |

supplementary materials

| | | | | |
|-----|--------------|--------------|-------------|------------|
| H2 | -0.6479 | 0.4145 | 0.1688 | 0.040* |
| N3 | -0.4509 (3) | 0.57078 (10) | 0.17064 (9) | 0.0340 (3) |
| N4 | 0.1919 (3) | 0.59882 (10) | 0.35853 (9) | 0.0351 (4) |
| N5 | 0.4505 (3) | 0.87609 (10) | 0.41396 (9) | 0.0325 (3) |
| N6 | 0.6992 (3) | 0.88485 (10) | 0.52872 (9) | 0.0357 (4) |
| H6A | 0.8182 | 0.9042 | 0.5670 | 0.043* |
| C11 | 0.02168 (14) | 0.36102 (3) | 0.38240 (3) | 0.0529 (2) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|--------------|-------------|
| C1 | 0.0312 (8) | 0.0258 (8) | 0.0273 (9) | 0.0014 (6) | 0.0001 (6) | -0.0027 (7) |
| C2 | 0.0335 (8) | 0.0243 (8) | 0.0244 (9) | 0.0013 (6) | -0.0012 (6) | -0.0004 (6) |
| C3 | 0.0414 (9) | 0.0262 (9) | 0.0291 (9) | -0.0002 (7) | -0.0047 (7) | 0.0041 (7) |
| C4 | 0.0457 (10) | 0.0258 (9) | 0.0344 (10) | -0.0026 (7) | -0.0026 (7) | 0.0009 (7) |
| C5 | 0.0339 (8) | 0.0264 (9) | 0.0277 (9) | 0.0022 (7) | -0.0018 (6) | -0.0023 (8) |
| C6 | 0.0470 (10) | 0.0275 (9) | 0.0297 (10) | 0.0045 (7) | -0.0016 (7) | 0.0042 (7) |
| C7 | 0.0680 (13) | 0.0322 (11) | 0.0498 (14) | 0.0004 (10) | -0.0272 (10) | 0.0014 (9) |
| C8 | 0.0321 (8) | 0.0318 (9) | 0.0389 (10) | -0.0054 (7) | -0.0013 (7) | -0.0069 (8) |
| C9 | 0.0321 (8) | 0.0321 (9) | 0.0366 (10) | -0.0037 (7) | -0.0003 (7) | -0.0046 (8) |
| C10 | 0.0294 (7) | 0.0277 (9) | 0.0311 (9) | 0.0024 (6) | -0.0005 (6) | -0.0029 (7) |
| C11 | 0.0395 (9) | 0.0298 (9) | 0.0323 (10) | 0.0011 (7) | -0.0025 (7) | 0.0004 (7) |
| C12 | 0.0386 (9) | 0.0283 (9) | 0.0376 (11) | -0.0030 (7) | -0.0036 (7) | -0.0024 (8) |
| N1 | 0.0408 (8) | 0.0250 (7) | 0.0327 (9) | 0.0002 (6) | 0.0004 (6) | -0.0001 (6) |
| N2 | 0.0387 (7) | 0.0285 (8) | 0.0312 (8) | -0.0022 (6) | -0.0069 (6) | -0.0021 (6) |
| N3 | 0.0415 (8) | 0.0282 (8) | 0.0301 (8) | 0.0048 (6) | -0.0060 (6) | 0.0008 (6) |
| N4 | 0.0407 (8) | 0.0257 (8) | 0.0359 (9) | -0.0009 (6) | -0.0090 (6) | -0.0031 (6) |
| N5 | 0.0349 (7) | 0.0303 (8) | 0.0305 (8) | -0.0009 (6) | -0.0048 (6) | -0.0002 (6) |
| N6 | 0.0390 (8) | 0.0320 (8) | 0.0331 (9) | -0.0011 (6) | -0.0094 (6) | -0.0062 (7) |
| C11 | 0.0763 (4) | 0.0314 (3) | 0.0444 (3) | -0.0069 (2) | -0.0233 (3) | 0.0115 (2) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-------------|---------|-----------|
| C1—N1 | 1.355 (2) | C7—H7C | 0.9700 |
| C1—N4 | 1.355 (2) | C8—N4 | 1.468 (2) |
| C1—C2 | 1.434 (2) | C8—C9 | 1.531 (3) |
| C2—C5 | 1.427 (2) | C8—H8A | 0.9800 |
| C2—C3 | 1.457 (2) | C8—H8B | 0.9800 |
| C3—C4 | 1.359 (3) | C9—C10 | 1.499 (2) |
| C3—C11 | 1.7360 (18) | C9—H9A | 0.9800 |
| C4—N2 | 1.363 (2) | C9—H9B | 0.9800 |
| C4—H4 | 0.9400 | C10—C11 | 1.362 (2) |
| C5—N3 | 1.349 (2) | C10—N5 | 1.385 (2) |
| C5—N2 | 1.355 (2) | C11—N6 | 1.374 (2) |
| C6—N3 | 1.321 (2) | C11—H11 | 0.9400 |
| C6—N1 | 1.331 (2) | C12—N5 | 1.320 (2) |
| C6—H6 | 0.9400 | C12—N6 | 1.342 (2) |
| C7—N4 | 1.446 (3) | C12—H12 | 0.9400 |
| C7—H7A | 0.9700 | N2—H2 | 0.8700 |

| | | | |
|------------|-------------|-------------|-------------|
| C7—H7B | 0.9700 | N6—H6A | 0.8700 |
| N1—C1—N4 | 114.64 (15) | H8A—C8—H8B | 107.8 |
| N1—C1—C2 | 119.20 (15) | C10—C9—C8 | 111.87 (14) |
| N4—C1—C2 | 126.15 (16) | C10—C9—H9A | 109.2 |
| C5—C2—C1 | 113.83 (15) | C8—C9—H9A | 109.2 |
| C5—C2—C3 | 102.77 (14) | C10—C9—H9B | 109.2 |
| C1—C2—C3 | 143.40 (16) | C8—C9—H9B | 109.2 |
| C4—C3—C2 | 108.69 (15) | H9A—C9—H9B | 107.9 |
| C4—C3—C11 | 118.73 (14) | C11—C10—N5 | 109.35 (16) |
| C2—C3—C11 | 132.58 (14) | C11—C10—C9 | 128.54 (17) |
| C3—C4—N2 | 109.48 (16) | N5—C10—C9 | 122.03 (16) |
| C3—C4—H4 | 125.3 | C10—C11—N6 | 106.29 (16) |
| N2—C4—H4 | 125.3 | C10—C11—H11 | 126.9 |
| N3—C5—N2 | 123.13 (15) | N6—C11—H11 | 126.9 |
| N3—C5—C2 | 126.66 (16) | N5—C12—N6 | 112.00 (17) |
| N2—C5—C2 | 110.21 (15) | N5—C12—H12 | 124.0 |
| N3—C6—N1 | 128.55 (17) | N6—C12—H12 | 124.0 |
| N3—C6—H6 | 115.7 | C6—N1—C1 | 119.29 (15) |
| N1—C6—H6 | 115.7 | C5—N2—C4 | 108.84 (15) |
| N4—C7—H7A | 109.5 | C5—N2—H2 | 125.6 |
| N4—C7—H7B | 109.5 | C4—N2—H2 | 125.6 |
| H7A—C7—H7B | 109.5 | C6—N3—C5 | 112.45 (15) |
| N4—C7—H7C | 109.5 | C1—N4—C7 | 123.13 (16) |
| H7A—C7—H7C | 109.5 | C1—N4—C8 | 121.64 (15) |
| H7B—C7—H7C | 109.5 | C7—N4—C8 | 115.03 (15) |
| N4—C8—C9 | 112.60 (15) | C12—N5—C10 | 105.27 (16) |
| N4—C8—H8A | 109.1 | C12—N6—C11 | 107.09 (15) |
| C9—C8—H8A | 109.1 | C12—N6—H6A | 126.5 |
| N4—C8—H8B | 109.1 | C11—N6—H6A | 126.5 |
| C9—C8—H8B | 109.1 | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| N2—H2···N5 ⁱ | 0.87 | 1.98 | 2.845 (2) | 175 |
| N6—H6A···N3 ⁱⁱ | 0.87 | 2.04 | 2.892 (2) | 167 |

Symmetry codes: (i) $-x-1/2, y-1/2, -z+1/2$; (ii) $x+3/2, -y+3/2, z+1/2$.

Fig. 1

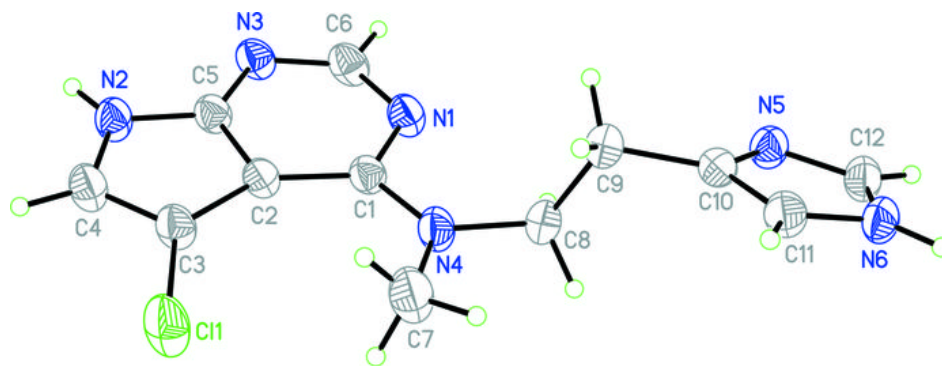


Fig. 2

